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Rank Xerox (UK) Business Services
(3.10/3.09/3.3.3)

Liquid Crystal polymers. I. Preparation and properties of p-Hydroxybenzoic Acid Copolyesters

Description

The present invention relates to a melt-processable polyester resin composition capable of forming an anisotropic molten phase, said composition being superior in mechanical and thermal properties.

A melt-processable polyester capable of forming an anisotropic molten phase (referred to as liquid-crystalline polyester hereinafter) is an entirely new material attracting attention on account of its outstanding performance including thermal properties, heat stability, chemical resistance, ease of moulding, small moulding shrinkage, and low coefficient of linear expansion. Because of these features, it is finding use as audio equipment parts, automotive parts, and electrical parts.

The liquid crystalline polyester can be processed as such into the above-mentioned articles but is more often used in combination with a variety of reinforcing materials or fillers with the object of improving the properties of the articles. There is still room for further improvement in the mechanical properties and thermal stability of such articles and also in filler handling.

It is known in the state of the art that other resins than liquid crystalline polymers, such as polybutylene phthalate, may be blended with a filler and a surface-treating agent such as an epoxy resin and polyvinyl alcohol.

The invention relates to an improvement of the liquid crystalline polymer in view of mechanical strength and thermal stability without impairing other physical properties thereof and then the blending operation of a filler.

A polyester composition of the invention comprises a polyester having the anisotropic phase, 1 to 70 percent by weight, based on the composition, of a filler other than a polyamide and 0.05 to 10 percent by weight, based on the filler, of a polyamide. The polyamide serves to collect or treat on the surface the filler. In order to enhance the effect of the invention, it is preferable that the filler is treated with the polyamide and then the mixture is blended with the polyester. Accordingly the filler gets easier to treat in the blending step.

Accordingly, it is an object of the present invention to provide a polyester resin composition which comprises a melt-processable polyester capable of forming an anisotropic molten phase, a filler, and a polyamide resin as a surface treating agent, Collecting agent, or additive. A further object of the present invention is a method of producing a polyester composition which comprises of liquid crystalline polyester and 1 to 70 percent by weight, based on the composition, of a filler other than a polyamide characterized in that the filler has been surface treated with 0,05 to 20% by weight, based on the weight of filler, of a polyamide and the surface treated filler is then incorporated in the composition.

The liquid-crystalline polyester used in the invention is a melt-processable polyester having such characteristic properties that the polymer molecule chains are regularly oriented parallel to one another in the molten state. The state in which molecules are oriented in this manner is referred to as the liquid-crystal state or the nematic phase of liquid crystal substance. A polymer like this is composed of monomers which are long and narrow, flat, and rigid along the long axis of the molecule and have a plurality of chain extension bonds coaxial or parallel to one another.

The properties of the anisotropic molten phase can be determined by the ordinary polarization test using crossed nicols. More particularly, the properties can be determined with a Leitz polarizing microscope of 40 magnifications by observing a sample placed on a Leitz hot stage in a nitrogen atmosphere. The polymer is optically anisotropic. Namely, it transmits a light when it is placed in between the crossed nicols. When the sample is optically anisotropic, the polarized light can be transmitted through it even in a still state.

The constituents of the polymer forming the above-mentioned anisotropic molten phase are as follows:

(1) one or more of aromatic and alicyclic dicarboxylic acids,
(2) one or more of aromatic, alicyclio, and aliphatic diols,
(3) one or more of aromatic hydroxycarboxylic acids,
(4) one or more of aromatic thiolcarboxylic acids,
(5) one or more of aromatic dithiols and aromatic thiolphenols, and
(6) one or more of aromatic hydroxyamines and aromatic diamines.

The polymers forming the anisotropic molten phase comprise the following combinations:

I) a polyester comprising (1) and (2),
II) a polyester comprising only (3),
III) a polyester comprising (1), (2), and (3),
IV) a polythiol ester comprising only (4),
V) a polythiol ester comprising (1) and (5),
VI) a polythiol ester comprising (1), (4), and (5),

VII) a polyester amide comprising (1), (3), and (6), and

VIII) a polyesteramide comprising (1), (2), (3), and (6).

The polymers (I) to (VIII) comprising the above-mentioned components may be divided into a group of those capable of forming the anisotropic molten phase and a group of those incapable of forming said phase according to the constituents, polymers composition, and sequence distribution. The polymers used in the present invention are limited to those of the former group.

In addition to the above-mentioned combinations of the components, the polymers forming the anisotropic molten phase include also aromatic polyazomethines such as poly(nitrilo-2-methyl-1,4-phenylenenitriloethylidine-1,4-phenylenethylidine), poly(nitrilo-2-methyl-1,4-phenylenenitrilomethylidine-1,4-phenylenemethylidine) and poly(nitrilo-2-chloro-1,4-phenylenenitrilomethylidine-1,4-phenylenemethylidine).

Further, in addition to the above-mentioned combinations of the components, the polymers forming the anisotropic molten phase include polyester carbonates essentially comprising 4-hydroxybenzoyl, dihydroxyphenyl, dihydroxycarbonyl, and terephthaloyl units.

Examples of the compounds constituting the above-mentioned polymers I) to VIII) include aromatic dicarboxylic acids such as terephthalic acid, 4,4'-diphenyldicarboxylic acid, 4,4'-triphenyldicarboxylic acid, 2,6-naphthalenedicarboxylic acid, diphenyl ether-4,4'-dicarboxylic acid, diphenoxyethane-4,4'-dicarboxylic acid, dipheloxybutane-4,4'-dicarboxylic acid, diphenylethane-4,4'-dicarboxylic acid, isophthalic acid, diphenyl ether-3,3'-dicarboxylic acid, diphenoxyethane-3,3'-dicarboxylic acid, diphenylethane-3,3'-dicarbbxylic acid, and naphthalene-1,6-dicarboxylicacid; and those substituted with alkyl and alkoxy groups and halogen atoms, such as chloroterephthalic acid, dichloroterephthalic acid, bromoterephthalic acid, methylterephthalic acid, dimethylterephthalic acid, ethylterephthalic acid, methoxyterephthalic acid, and ethoxyterephthalic acid.

Examples of the alicyclic dicarboxylic acids include trans-1,4-cyclohexanedicarboxylic acid, cis-1,4-cyclohexanedicarboxylic acid, and 1,3-cyclohexanedicarboxylic acid as well as those substituted with alkyl and alkoxy groups and halogen atoms, such as trans-1,4-(1-methyl)cyclohexane dicarboxylic acid and trans-1,4-(1-chloro)cyclohexanedicarboxylic acid.

Examples of the aromatic diols include hydroquinone, resorcinol, 4,4′-dihroxydiphenyl, 4,4′-dihydroxytriphenyl, 2,6-naphthalenediol, 4,4′-dihydroxydiphenyl ether, bis-(4-hydroxyphenoxy)ethane, 3,3′-dihydroxydiphenyl, 3,3′-dihydroxydiphenyl ether, 1,6-naphthalenediol, 2,2-bis(4-hydroxyphenyl)propane, and 2,2-bis-(4-hydroxyphenyl)methane as well as those substituted with alkyl and alkoxy groups and halogen atoms, such as chlorohydroquinone, methylhydroquinone, 1-butylhydroquinone, phenylhydroquinone, methoxyhydroquinone, 1-butylhydroquinone, phenylhydroquinone, methoxyhydroquinone, phenoxyhydroquinone, 4-chlororesorcinol, and 4-methylresorcinol.

Examples of the alicyclic diols include trans-1,4-cyclohexanediol, cis-1,4-cyclohexanediol, trans-1,4-cyclohexanedimethanol, cis-1,4-cyclohexanedimethanol, trans-1,3-cyclohexanediol, cis-1,2-cyclohexanediol, and trans-1,3-cyclohexanedimethanol as well as those substituted with alkyl and alkoxy groups and halogen atoms, such as trans-1,4-(1-methyl)cyclohexanediol and trans-1,4-(1-chloro)cyclohexanediol.

Examples of the aliphatic diols include straight-chain or branched-chain aliphatic diols such as ethylene glycol, 1,3-propanediol, 1,4-butanediol, and neopentyl glycol.

Examples of the aromatic hydroxycarboxylic acids include 4-hydroxybenzoic acid, 3-hydroxybenzoic acid, 6-hydroxy-2-naphthoic acid, and 6-hydroxy-1-naphthoic acid as well as those substituted with alkyl and alkoxy groups and halogen atoms, such as 3-methyl-4-hydroxybenzoic acid, 3,5-dimethyl-4-hydroxybenzoic acid, 2,6-dimethyl-4-hydroxbenzoic acid, 3-methoxy-4-hydroxybenzoic acid, 3,5-dimethoxy-4-hydroxybenzoic acid, 6-hydroxy-5-methyl-2-naphthoic acid, 6-hydroxy-5-methoxy-2-naphthoic acid, 3-chloro-4-hydroxybenzoic acid, 2-chloro-4-hydroxy-benzoic acid, 2,3-dichloro-4-hydroxybenzoic acid, 3,5-dichloro-4-hydroxybenzoic acid, 2,5-dichloro-4-hydroxybenzoic acid, 3-bromo-4-hydroxybenzoic acid, 6-hydroxy-5-chloro-2-naphthoic acid, 6-hydroxy-7-chloro-2-naphthoic acid, and 6-hydroxy-5,7-dichloro-2-naphthoic acid.

Examples of the aromatic mercaptocarboxylic acids include 4-mercaptobenzoic acid, 3-mercaptobenzoic acid, 6-mercapto-2-naphthoic acid, and 7-mercapto-2-naphthoic acid.

Examples of the aromatic dithiols include benzene-1,4-dithiol, benzene-1,3-dithiol, 2,6-naphthalenedithiol, and 2,7-naphthalenedithiol.

Examples of the aromatic mercaptophenols include 4-mercaptophenol, 3-mercaptophenol, 6-mercaptophenol, and 7-mercaptophenol.

Examples of the aromatic hydroxamines and aromatic diamines include 4-aminophenol, N-methyl-4-aminophenol, 1,4-phenylenediamine, N-methyl-1,4-phenylenediamine, N,N'-dimethyl-1,4-phenylenediamine, 3-aminophenol, 3-methyl-4-aminophenol, 2-chloro-4-aminophenol, 4-amino-1-naphthol, 4-amino-4'-hydroxydiphenyl, 4-amino-4'-hydroxydiphenyl ether, 4-amino-4'-hydroxyphenylmethane, 4-amino-4'-hydroxydiphenyl sulfide, 4,4'-diaminophenyl sulfide (thiodianiline), 4,4'-diaminodiphenyl sulfone, 2,5-diaminotoluene, 4,4'-ethylenedianiline, 4,4'-diaminodiphenoxyethane, 4,4'-diaminodiphenylmethane (methylenedianiline), and 4,4'-diaminodiphenyl ether (oxydianiline).

Among the polymers capable of forming the anisotropic molten phase suitably used in the present invention, the polyesters (I), (II), and (III), and polyesteramides (VIII) can be prepared by various ester forming processes wherein organic monomers each having a functional group which can form a desired recurring unit by the condensation are reacted with each other. The functional groups of these organic monomers include carboxyl, hydroxyl, ester, acryloxy, acyl halide, and amine groups. These organic monomers can be reacted by melt acidolysis in the absence of any heat exchange fluid. In this process, the monomers are heated to form a melt. As the reaction proceeds, the solid polymer particles are suspended in the melt. In the final stage of the condensation reaction, the reaction system may be evacuated to facilitate the removal of volatile by-products (e.g., acetic acid and water).

A slurry polymerization process may also be employed in the preparation of fully aromatic polyesters suitable for use in the present invention. In this process, the solid product is obtained in the form of suspension thereof in a heat exchange medium.

In either of said melt acidolysis and slurry polymerization processes, organic monomeric reactants from which fully aromatic polyesters can be derived may be employed in the reaction in a modified form obtained by esterifying the hydroxyl group of the monomer at ambient temperature (i.e., in the form of their lower acyl esters). The lower acyl groups have preferably about 2 to 4 carbon atoms. Preferably, acetates of the organic, monomeric reactants are employed in the reaction.

Typical examples of the catalysts usable in both of the melt acidolysis and slurry processes include dialkyltin oxides (such as dibutyltin oxide), diaryltin oxide, titanium dioxide, antimony trioxide, alkoxytitanium silicates, titanium alkoxides, alkali metal and alkaline earth metal salts of carboxylic acids (such as zinc acetate), Lewis acids (such as BF_3), and gaseous acid catalysts such as hydrogen halides (e.g., HCl). The catalyst is used in an amount of about 0.001-1 wt%, particularly about 0.01-0.2 wt%, based on the total weight of the monomer.

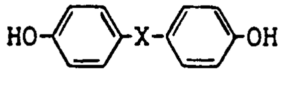
The fully aromatic polymers suitable for use in the present invention are substantially insoluble in ordinary solvents and, therefore, they are unsuitable for use by solution processing. However, as described above, these polymers can be processed easily by an ordinary melt processing process. Particularly preferred fully aromatic polymers are soluble in pentafluorophenol to some extent.

The fully aromatic polyester preferably used in the present invention have a weight-average molecular weight of generally about 2,000-200,000, preferably about 10,000-50,000, particularly about 20,000-25,000. The fully aromatic polyesteramides preferably used have a molecular weight of generally about 5,000-50,000, preferably about 10,000-30,000, for example, 15,000-17,000. The molecular weight may be determined by gel permeation chromatography or other standard methods in which no polymer solution is formed, such as a method in which terminal groups of a compression-molded film are determined by infrared spectroscopy. In another method, the molecular weight of the polymer may be determined according to a light-scattering method after it is dissolved in pentafluorophenol.

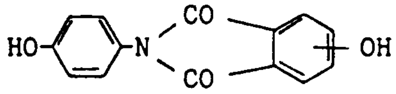
When the fully aromatic polyester or polyesteramide is dissolved in pentafluorophenol at 60 ° C to obtain a 0.1 wt% solution thereof, the solution has generally an inherent viscosity (I.V.) of at least about 2.0 dl/g, for example, about 2.0-10.0 dl/g.

The anisotropic molten phase-forming polyesters used in the present invention should preferably be aromatic polyesters and aromatic polyester amides. Other preferred examples include those polyesters containing aromatic polyester and aromatic polyesteramide in the same molecular chain.

They are constructed of those compounds which are exemplified by naphthalene compounds such as 2,6-naphthalene dicarboxylic acid, 2,6-dihydroxynaphthalene, 1,4-dihydoxyhaphthalene, and 6-hydroxy-2-naphthoic acid; biphenyl compounds such as 4,4′-diphenyldicarboxylic acid and 4,4′-dihydroxybiphenyl; compounds represented by the following formula (I), (II), or (III).



(I)



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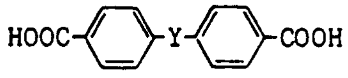


(III)

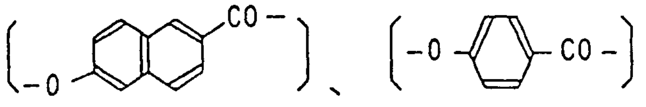
(where X is a group selected from C_1-C_4 alkylene, alkylidene, -O-, -SO-, -SO_2-, -S-, and -CO-, and Y is a group selected from -$(CH_2)_n$- (n = 1-4) and -$O(CH_2)_nO$- (n = 1-4).); para-substituted benzene compounds such as p-hydroxybenzoic acid, terephthalic acid, hydroquinone, p-aminophenol, and p-phenylenediamine, and nucleus-substituted benzene compounds (the substituent group being selected from chlorine, bromine, methyl, phenyl, and 1-phenylethyl); and meta-substituted benzene compounds such as isophthalic acid and resorcinol.

Preferred examples of polyesters partially containing the above-mentioned constituents in the same molecular chain include polyalkylene terephthalate, with the alkyl group containing 2-4 carbon atoms.

Those polyesters containing one or more than one kind of the above-mentioned naphthalene compounds, biphenyl compounds, para-substituted benzene compounds are particularly preferable. Among the para-substituted benzene compounds, p-hydroxybenzoic acid, methyl hydroquinone, and 1-phenylethylhydroquinone are particularly preferable.

The combination of the constituents are exemplified as follows:

1)



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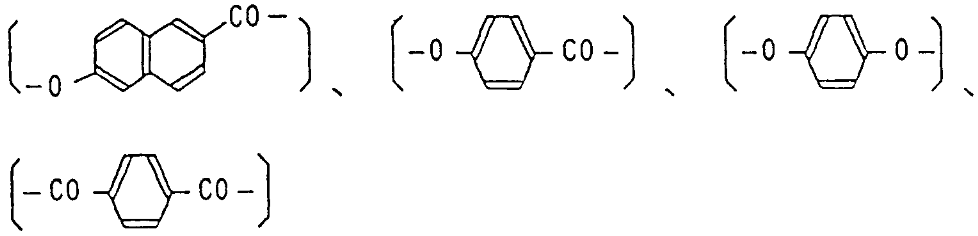

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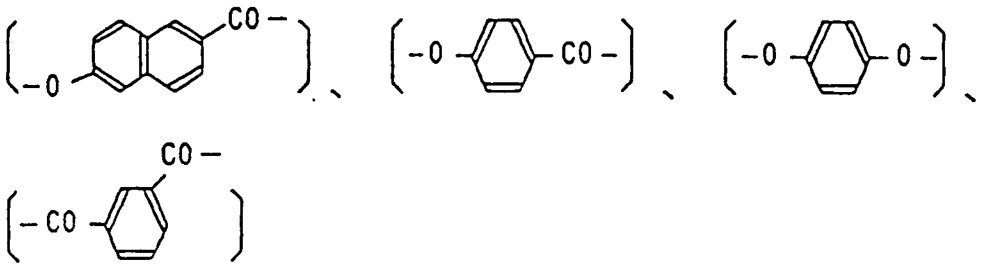

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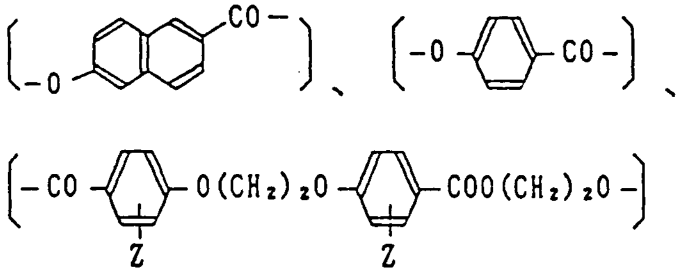

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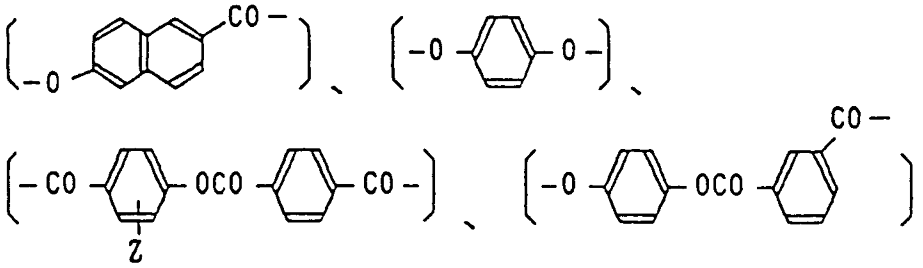

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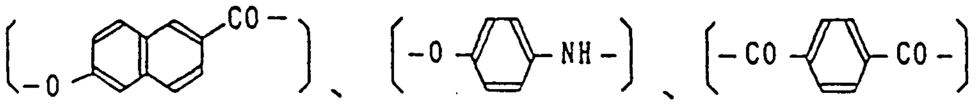

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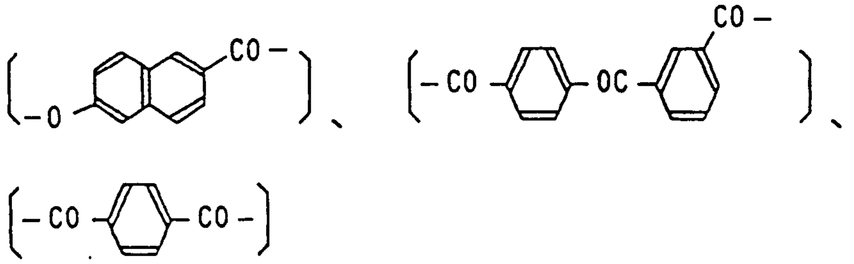

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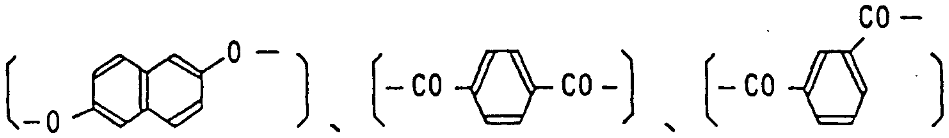

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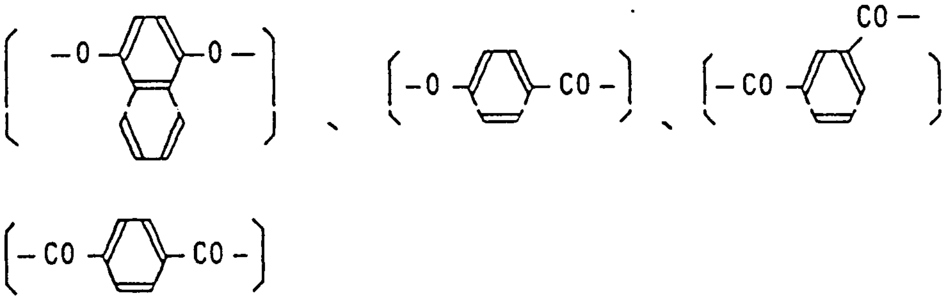

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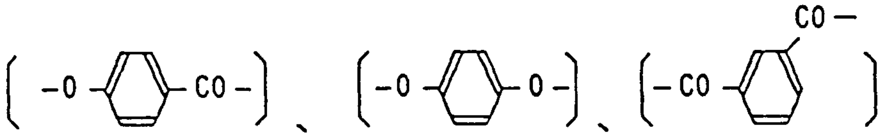

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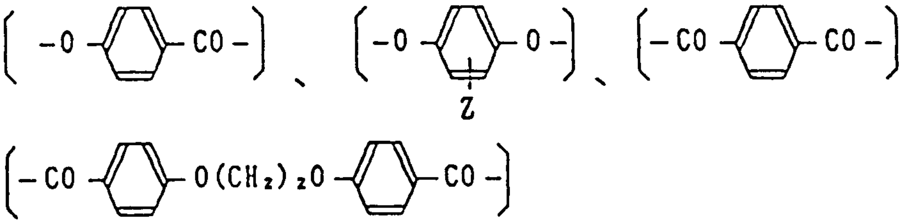

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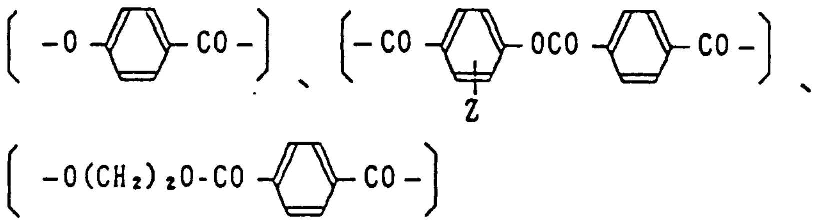

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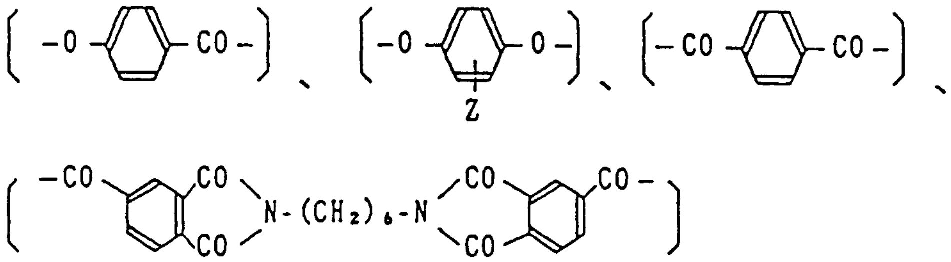

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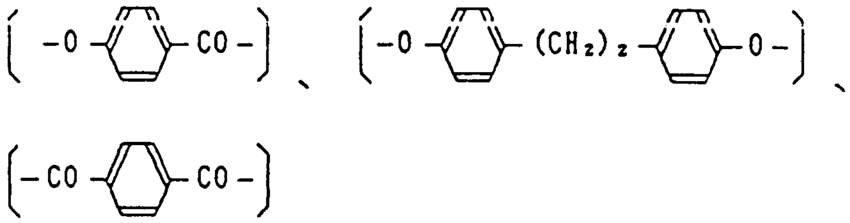

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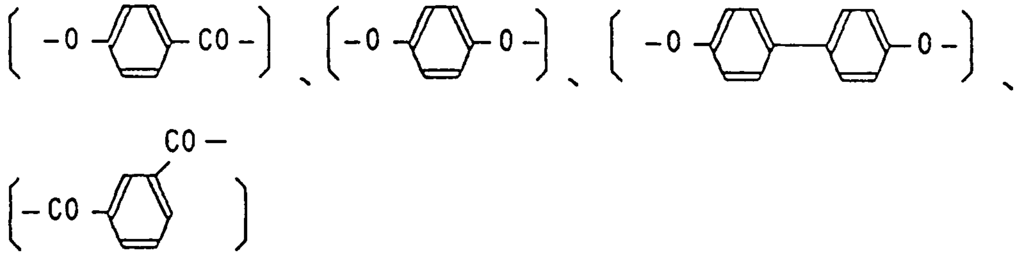

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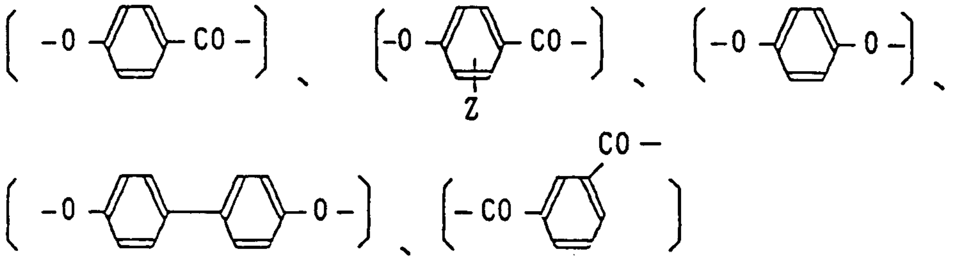

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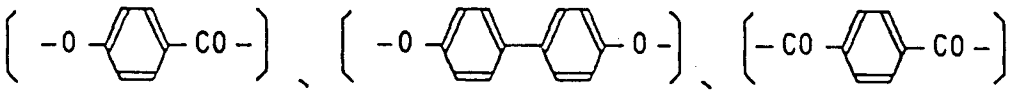

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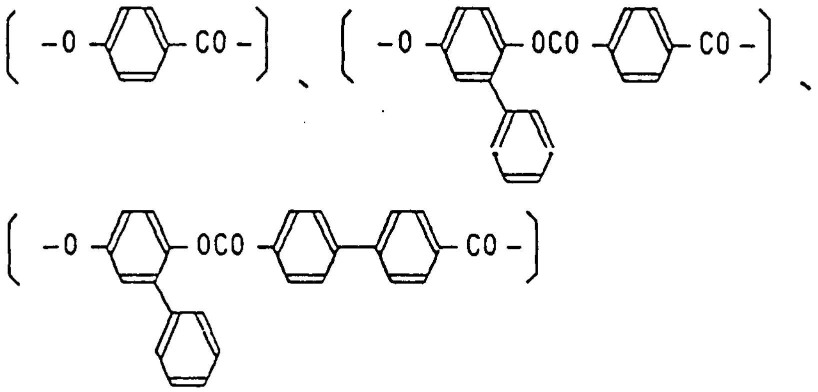

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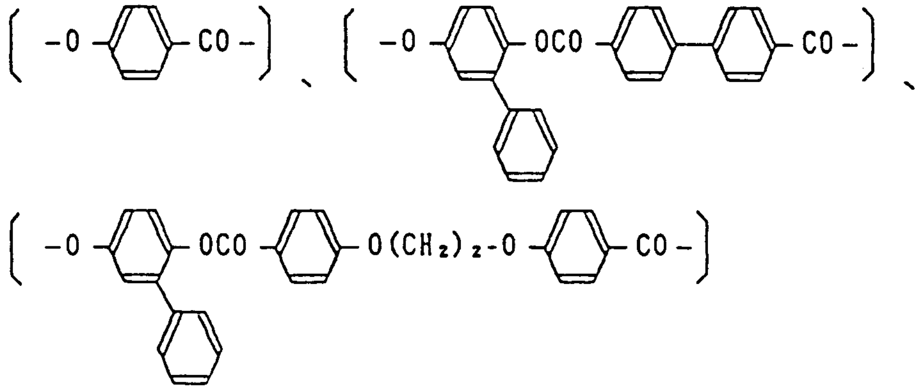

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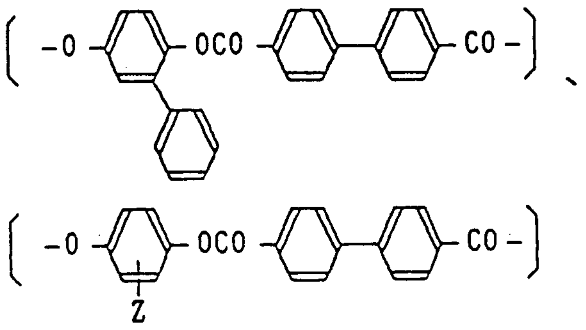

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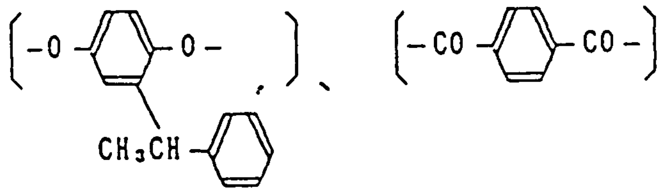

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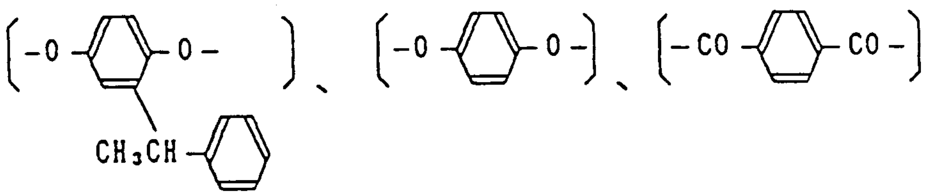

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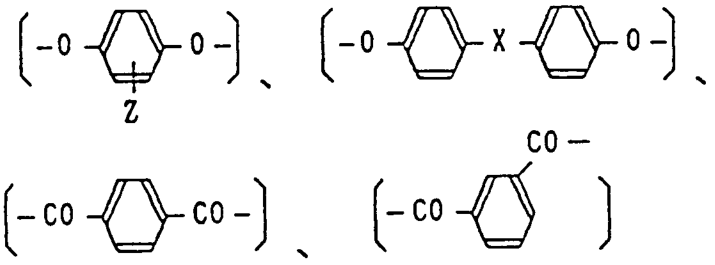

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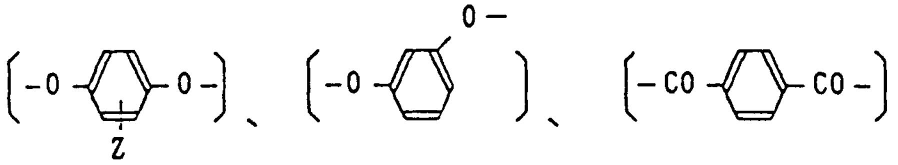

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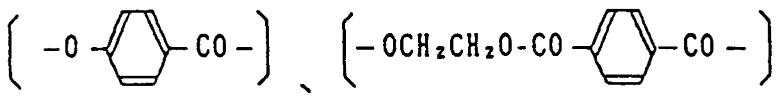

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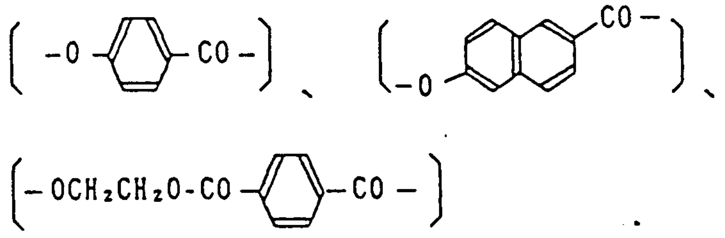

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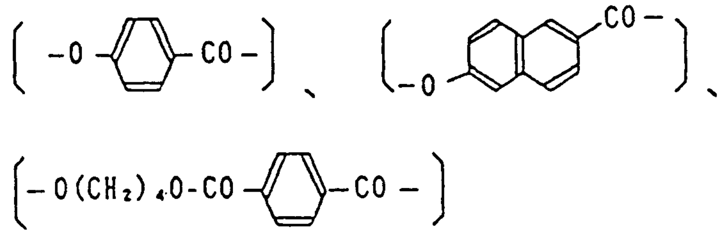
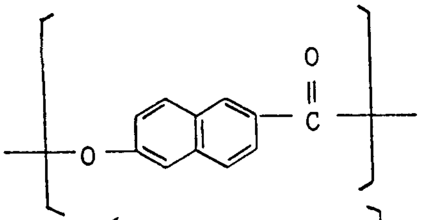


In the formulas, Z is a substituent group selected from -Cl, -Br, and $-CH_3$, and X is a substituent group selected from C_1-C_4 alkylene, alkylidene, -O-, -SO-, $-SO_2-$, -S-, and -CO-.

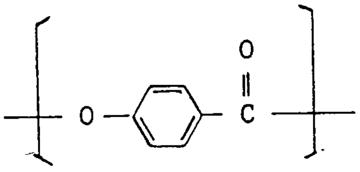
The particularly preferred anisotropic molten phase-forming polyesters used in the present invention are those containing at least about 10 mol% of a naphthalene moiety-containing recurring unit such as 6-hydroxy-2-naphthoyl, 2,6-dihydroxynaphthalene, and 2,6-dicarboxynaphthalene. Preferred polyesteramides are those having recurring units each comprising the above-mentioned naphthalene moiety and 4-aminophenol or 1,4-phenylenediamine moiety. Their examples are shown below.

(1) Polyester essentially comprising the following recurring units I and II:

I



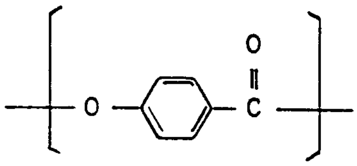
II



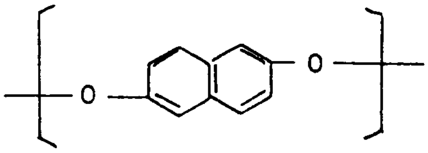
This polyesters comprises about 10-90 mol% of unit I and about 10-90 mol% of unit II. In one embodiment, the amount of unit I is 65-85 mol%, preferably 70-80 mol% (for example, about 75 mol%). In another embodiment, the amount of unit II is 15-35 mol%, preferably 20-30 mol%. At least a portion of the hydrogen atoms attaching directly to the ring may be replaced with a substituent group selected from the group consisting of alkyl groups having 1-4 carbon atoms, alkoxy groups having 1-4 carbon atoms, halogen atoms, a phenyl group, substituted phenyl groups, and combinations thereof.

(2) Polyester essentially comprising the following recurring units I, II, and III:

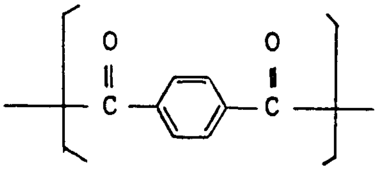
I



II



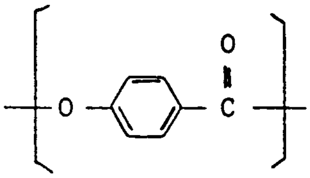
III



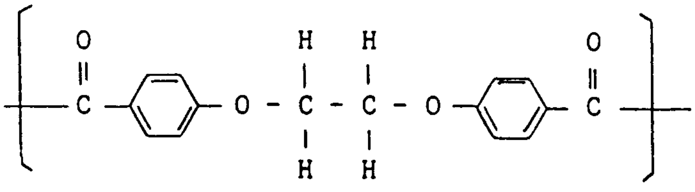
This polyester contains about 30-70 mol% of unit I. It comprises preferably about 40-60 mol% of unit I, about 20-30 mol% of unit II, and about 20-30 mol% of unit III. At least a portion of the hydrogen atoms attaching directly to the ring may be replaced with a substituent group selected from the group consisting of alkyl groups having 1-4 carbon atoms, alkoxy groups having 1-4 carbon atoms, halogen atoms, a phenyl group, substituted phenyl groups, and combinations thereof.

(3) Polyester essentially comprising the following recurring units I, II, III, and IV.

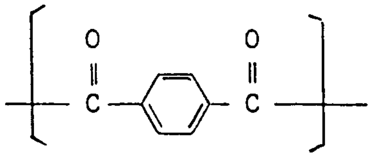
I



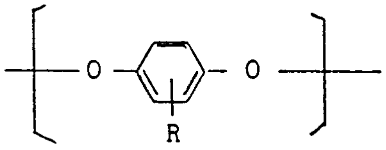
II



III



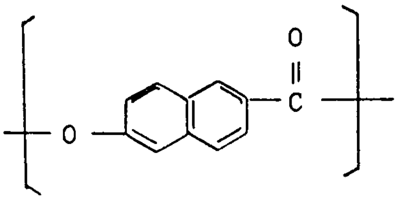
IV



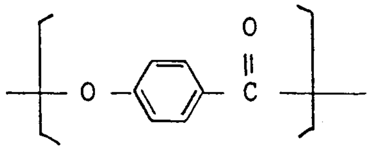
(wherein R represents a substituent for the hydrogen atom on the aromatic ring which is methyl, chlorine, bromine, or a combination thereof.) This polyester contains 20-60 mol% of unit I, 5-18 mol% of unit II, 5-35 mol% of Unit II, and 20-40 mol% of unit IV. Preferably, it comprises 35-45 mol% of unit I, 10-15 mol% of unit II, 15-25 mol% of unit II, and 25-35 mol% of unit IV, provided that the total molar concentration of units II and III is substantially equal to that of unit IV. At least a portion of the hydrogen atoms attaching directly to the ring may be replaced with a substituent group selected from the group consisting of alkyl groups having 1-4 carbon atoms, alkoxy groups having 1-4 carbon atoms, halogen atoms, a phenyl group, substituted phenyl groups, and a combination thereof. When the fully aromatic polyester is dissolved in pentafluorophenol at 60 °C to obtain a 0.3 w/v% solution thereof, the solution has generally an inherent viscosity of at least 2.0 dl/g, for example, 2.0-10.0 dl/g.

(4) Polyester essentially comprising the following recurring units I, II, III, and IV:

I

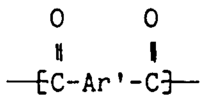


II



III dioxyaryl unit of the general formula: $\{\text{O-Ar-O}\}$ wherein Ar represents a divalent group having at least one aromatic ring,

IV dicarboxyaryl unit of the general formula:



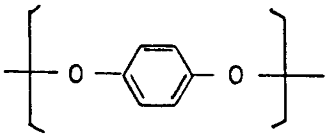
$$-\!\{\overset{\overset{\displaystyle O}{\|}}{C}\text{-Ar'-}\overset{\overset{\displaystyle O}{\|}}{C}\}\!-$$

wherein Ar' represents a divalent group having at least one aromatic ring.

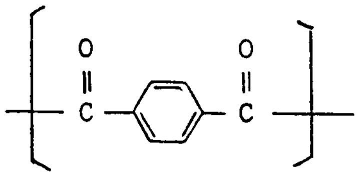
The amount of unit I is 20-40 mol%. The amount of unit II is in excess of 10 mol% but up to 50 mol%. The amount of unit III is in excess of 5 mol% but up to 30 mol% and the amount of unit IV is in excess of 5 mol% but up to 30 mol%. This polyester comprises preferably 20-30 mol% (for example, 25 mol%) of unit I, 25-40 mol% (for example 35 mol%) of unit II, 15-25 mol% (for example 20 mol%) of unit III and 15-25 mol% (for example 20 mol% of unit IV. If necessary, at least a portion of the hydrogen atoms attaching directly to the ring may be replaced with a substituent group selected from the group consisting of alkyl groups having 1-4 carbon atoms, alkoxy groups having 1-4 carbon atoms, halogen .... atoms, a phenyl group, substituted phenyl groups, and a combination thereof.

The units III and IV should preferably be symmetrical in the sense that the divalent bonds connecting them to adjacent units (on both sides) are arranged symmetrically on one or more aromatic rings (for example, when they are on a naphthalene ring, they are arranged in positions para to each other or on diagonal rings). However, asymmetrical units derived from resorcinol and isophthalic acid may also be used.

A preferred dioxyaryl unit III is as follows:

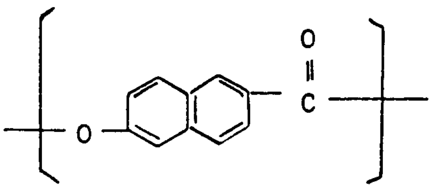


and a preferred dicarboxyaryl unit IV is as follows:



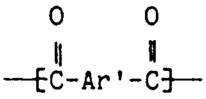
(5) Polyester essentially comprising the following recurring units I, II, and III:

I.



II. dioxyaryl unit of the general formula: $\{O\text{-}Ar\text{-}O\}$ wherein Ar represents a divalent group having at least one aromatic ring,

III. dicarboxyaryl unit of the general formula:

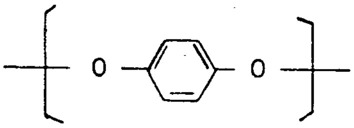


$$-\!\left[\overset{\overset{\displaystyle O}{\|}}{C}-Ar'-\overset{\overset{\displaystyle O}{\|}}{C}\right]\!-$$

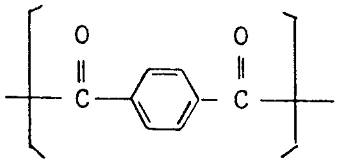
wherein Ar' represents a divalent group having at least one aromatic ring.

The amounts of units I, II, and III are 10-90 mol%, 5 to 45 mol% and 5-45 mol%, respectively. This polyester comprises preferably 20-80 mol% of unit I, 10-40 mol% of unit II, and 10-40 mol% of unit III. More preferably, it comprises about 60-80 mol% of unit I, 10-20 mol% of unit II and 10-20 mol% of unit III. If desired, at least a portion of the hydrogen atoms attaching directly to the ring may be replaced with a substituent group selected from the group consisting of alkyl group having 1-4 carbon atoms, alkoxy group having 1-4 carbon atoms, halogen atom, phenyl group, substituted phenyl group, and a combination thereof.

A preferred dioxyaryl unit II is as follows:

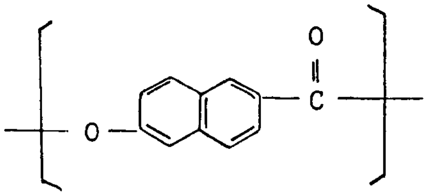


and a preferred dicarboxyaryl unit III is as follows:

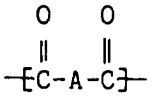


(6) Polyesteramide essentially comprising the following recurring units I, II, III, and IV:

I.



II. a unit of the general formula:



$$-\left[\overset{\overset{\displaystyle O}{\|}}{C}-A-\overset{\overset{\displaystyle O}{\|}}{C}\right]-$$

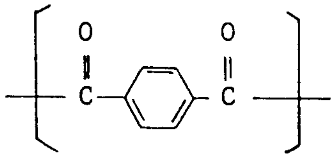
wherein A represents a divalent group having at least one aromatic ring or a divalent trans-cyclohexane group,

III. a unit of the general formula: [Y-Ar-Z] wherein Ar represents a divalent group having at least one aromatic ring, Y represent O, NH or NR, and Z represents NH or NR, R being an alkyl group having 1-6 carbon atoms or an aryl group,

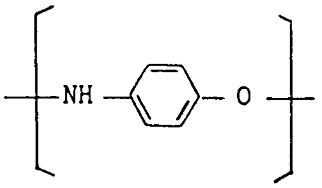
IV. a unit of the general formula: [O-Ar'-O] wherein Ar' represents a divalent group having at least one aromatic ring.

The amounts of units I, II, III, and IV are 10-90 mol%, 5-45 mol%, 5-45 mol%, and 0-40 mol%, respectively. If necessary, at least a portion of the hydrogen atoms attaching directly to the ring may be replaced with a substituent group selected from the group consisting of alkyl group having 1-4 carbon atoms, alkoxy group having 1-4 carbon atoms, halogen atom, phenyl group, substituted phenyl group, and a combination thereof.

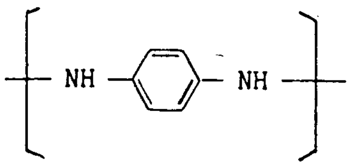
A preferred dicarboxyaryl unit II is as follows:



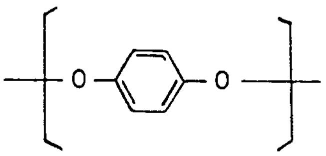
a preferred unit III is as follows:



or



and a preferred dioxyaryl unit IV is as follows:



The anisotropic molten phase-forming polymers of the present invention include also those wherein part of a polymer chain comprises a segment of the above-mentioned anisotropic molten phase-forming polymer and the balance comprises a segment of a thermoplastic resin which does not form an anisotropic molten phase.

The composition of the invention may be incorporated with various kinds of fillers for thermoplastic resins and thermosetting resins according to the intended applications. Examples of inorganic fillers include inorganic fibers such as glass fiber, carbon fiber, metallic fiber, ceramic fiber, boron fiber, potassium titanate fiber, and asbestos; powdery substances such as calcium carbonate, highly dispersible silicate, alumina, aluminum hydroxide, talc, clay, mica, glass flake, glass powder, glass beads, quartz sand, silica sand, wollastonite, metal powder, carbon black, barium sulfate, and calcined gypsum; granular and platy inorganic compounds such as silicon carbide, alumina, boron nitride, and silicon nitride; and whisker and metal whisker. Examples of fibrous fillers include fully aromatic polyester fibre; organic synthetic fiber such as phenolic resin fiber; and natural fibers such as cellulose fiber and jute. These fillers may be used individually or in combination with one another.

The filler should be added in an amount less than 70 wt% for good moldability. Particularly preferred fillers are PAN-based and pitch-based carbon filler.

According to the present invention, a polyamide resin is used as a surface-treating agent or collecting agent, . It is not specifically limited; but it includes nylon-6, nylon-66, nylon-11, nylon-12, copolymers thereof, and modified polyamides. A particularly preferred polyamide is a solvent-soluble nylon.

Examples of solvents for the nylon include alcohols, ketones, ethers, esters, aromatic hydrocarbons, and derivatives thereof. Preferred solvents are lower aliphatic alcohols such as methanol and ethanol.

Examples of the solvent-soluble nylon include commercial 6/66/610 terpolymer and 6/66/bis(4-aminocyclohexyl)methane-6 ("Ultramid" 1C, a product of BASF), which are produced by copolymerizing equal amounts of comonomers, and N-alkoxymethyl-modified nylon formed by reacting formalin and alcohol with nylon so that the hydrogen of the amide group is substituted.

The polyamide resin is incorporated into the composition in an amount of 0.05-20 wt% preferably 0.05-10 wt% based on the amount of the filler. Polyamide resin contents of less than 0.05 wt% do not produce the effect of the invention; polyamide resin contents in excess of 10 wt% may lower the heat distortion temperature of the moulded product. The most preferred amount is 0.5-7 wt%.

Whilst the polyamide resin produces the effect of the invention when it is incorporated as an additive into the liquid-crystalline polyester along with the filler, preferably, when it is incorporated into the composition in the form of a surface treating agent which has previously been applied to the surface of the filler the blending step is facilitated.

The surface treatment of the filler may be performed in the following manner.

(1) The polyamide resin is dissolved in a solvent, the solution is applied to the filler, and the solvent is removed.

(2) The polyamide resin is melted by heating, and the melt is applied to the filler. (Melt process)

It is also possible and desirable to use the polyamide in combination with known surface treating agents and collecting agents. They include functional compounds such as epoxy compounds, isocyanate compounds, silane compounds, and titanate compounds.

When the polyamide is incorporated in the composition as a separate additive, the resulting composite material has a high tensile strength, high modulus, and low coefficient of linear expansion. When the polyamide is incorporated in the composition in the form of a surface treating agent previously applied to the surface of the filler (eg. carbon fibre) the resulting composition is further improved in mechanical properties and thermal properties. The effect of surface treatment is remarkable in the case of PAN-based carbon fibre which has undergone oxidation treatment, because the polyamide firmly sticks to the carbon fibre and has a good affinity for the liquid-crystalline polyester. The polyamide resin used as a collecting agent greatly improves the handling characteristic of carbon fiber. Having a low bulk density, carbon fiber is difficult to incorporate into the liquid-crystalline polymer by melt-mixing with an extruder.

The composition of the invention may also contain known substances which are commonly added to thermoplastic resins and thermosetting resins. They are for example a plasticizer, anti-oxidant, UV light stabilizer, anti-static agent, flame retardant, dye and pigment lubricant (to improve flowability and releasability), and nucleating agent. They are used according to the performance required.

In addition, the liquid-crystalline polyester of the invention may be blended with any other thermoplastic resin within limits not deleterious to the object of the invention.

The thermoplastic resin that can be blended includes polyolefins such as polyethylene and polypropylene; aromatic polyester such as polyethylene terephthalate and polybutylene terephthalate (composed of aromatic dicarboxylic acid and diol or hydroxy carboxylic acid); polyacetal (homo- or copolymer), polystyrene, polyvinyl chloride, polycarbonate, ABS, polyoxyphenylene oxide, polyoxyphenylene sulfide, and fluoroplastic. These thermoplastic resins may be used in combination with one another.

The liquid crystalline polyester resin composition of the invention, which contains a filler and polyamide resin, has outstanding mechanical properties, thermal stability, low coefficient of molding shrinkage, and low coefficient of linear expansion, and superior performance. In addition, it can be easily handled when a filler is added.

The invention will be further illustrated by the following examples.

Examples 1 to 7 and Comparitive Examples 1 to 5

An aromatic polyester resin A (mentioned later) was mixed with a prescribed amount of filler and additive (for surface treatment or collecting) as shown in Table 1. The mixture was melted and formed into pellets by using an extruder. The pellets were dried by using a hot-air dryer at 140 °C until the water content was lower than 100 ppm. The dried pellets were molded into test pieces by using an injection molding machine. The resulting test pieces were examined for physical properties according to the following ASTM test methods. The results are shown in Table 1.

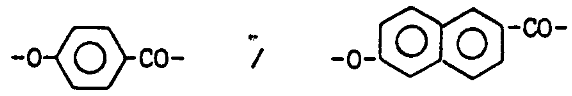
Tensile strength, tensile modulus, tensile elongation: ASTM D638
Flexural strength: ASTM D790
Izod impact strength: ASTM D256
Heat distortion temperature (18.6 kgf/cm^2): ASTM D648

It is noted from Table 1 that the composition of the invention is improved in mechanical properties, especially tensile modulus, flexural strength, and heat distortion temperature.

The same procedure as in Example 1 was repeated except that resin A was replaced by resins B, C, D, and E (mentioned later). The same results as in Example 1 were obtained.

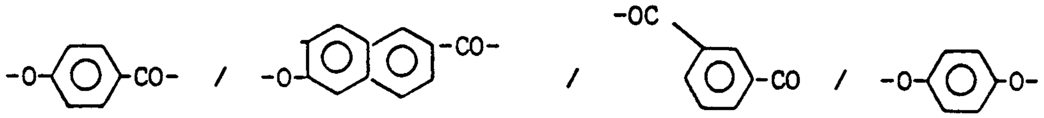
The resins A to E used in the examples have the following constituents.

A :



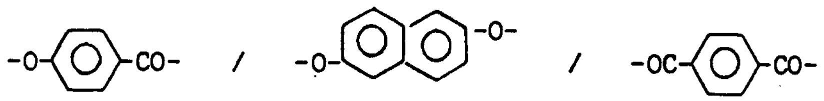
= 70/30

B :



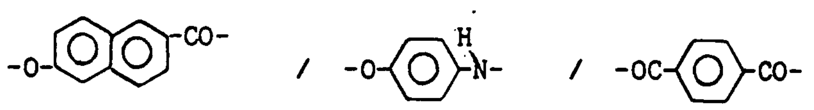
= 60/20/10/10

C :



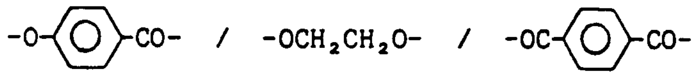
= 60/20/20

D :



= 70/15/15

E :



= 60/20/20

(The figures are in terms of molar ratio.)

Table 1

Example	Filler	Amount*1 (wt%)	Additive	Amount*2 (wt%)	Tensile strength (kgf/cm^2)	Tensile modulus (kgf/cm^2)	Tensile elongation (%)	Flexural strength (kg/cm^2)	Heat distortion temperature (°C)
1	Carbon fiber *3	30	Nylon copolymer *4	3.0	2000	30 × 10^4	1.3	2630	238
2	Carbon fiber *3	30	Nylon copolymer *4 (for collecting)	3.0	2210	32 × 10^4	1.3	2762	238
3	Carbon fiber *3	30	Nylon copolymer *4	8.5	2080	29 × 10^4	1.3	2590	223
4	Carbon fiber *3	30	Nylon-66	5.0	2071	29 × 10^4	1.3	2530	235
5	Carbon fiber *3	30	Nylon-6 (for surface treatment)	0.05	2059	30 × 10^4	1.2	2480	239
6	Glass fiber	30	Nylon copolymer *4	2.5	1540	16 × 10^4	1.7	2200	241
7	Wollastonite	15	Nylon copolymer *4	1.5	1900	13 × 10^4	4.0	1480	190
(1)	Carbon fiber	30	Epoxy resin	3.5	1710	28 × 10^4	1.1	2210	231
(2)	Carbon fiber	30	Polyvinyl alcohol	3.5	1680	28 × 10^4	1.1	2190	231
(3)	Glass fiber	30	Polyvinyl alcohol	2.5	1380	15.8 × 10^4	1.6	2090	238
(4)	Wollastonite	15	Aminosilane coupling agent for surface treatment)	0.05	1440	13 × 10^4	3.7	1400	186
(5)	--	--	--	--	2070	10 × 10^4	3.1	1560	182

( ) : Comparative Example

*1 : Amount (wt%) based on the total amount of the composition.

*2 : Amount (of additive for surface treatment or collecting) based on the amount of the filler.

*3 : Chopped strand produced by carbonizing acrylonitrile fiber.

*4 : Nylon-6/66/610 terpolymer.

Claims

1. A polyester composition which comprises a liquid crystalline polyester, 1 to 70 percent by weight, based on the composition, of a filler other than a polyamide and 0.05 to 10 percent by weight, based on the filler, of a polyamide.

2. A liquid crystalline polyester composition as claimed in claim 1, in which the filler is carbon fibre.

3. A liquid crystal polyester composition as claimed in claim 1, characterised in that the filler is selected from fully aromatic polyester fibres, organic synthetic fibres and natural fibres.

4. A method of producing a polyester composition which comprises a liquid crystalline polyester and, 1 to 70 percent by weight, based on the composition, of a filler other than a polyamide characterized in that the filler has been surface treated with 0,05 to 20% by weight, based on the weight of filler of a polyamide and the surface treated filler is then incorporated in the composition.

5. A method as claimed in claim 4, characterised in that 0.05 to 10 percent by weight of the polyamide based on the filler is used.

6. A method as claimed in claim 4 or 5, characterized in that the filler is carbon fibre.

7. A method as claimed in claim 4 or 5, characterised in that the filler is selected from fully aromatic polyester fibres, organic synthetic fibres and natural fibres.

Patentansprüche

1. Polyesterzusammensetzung, enthaltend einen flüssigkristallinen Polyester, 1 bis 70 Gew.-%, bezogen auf die Zusammensetzung, eines von Polyamid abweichenden Füllstoffs und 0,05 bis 10 Gew.-%, bezogen auf den Füllstoff, eines Polyamids.

2. Flüssigkristalline Polyesterzusammensetzung nach Anspruch 1, wobei es sich beim Füllstoff um Kohlenstoff-Fasern handelt.

3. Flüssigkristalline Polyesterzusammensetzung nach Anspruch 1, dadurch gekennzeichnet, daß der Füllstoff unter vollaromatischen Polyesterfasern, organischen Synthesefasern und natürlichen Fasern ausgewählt ist.

4. Verfahren zur Herstellung einer Polyesterzusammensetzung, die einen flüssigkristallinien Polyester und von 1 bis 70 Gew.-%, bezogen auf die Zusammensetzung, eines von Polyamid abweichenden Füllstoffs enthält, dadurch gekennzeichnet, daß der Füllstoff einer Oberflächenbehandlung mit 0,05 bis 20 Gew.-%, bezogen auf das Gewicht des Füllstoffs, eines Polyamids unterzogen wird und der oberflächenbehandelte Füllstoff der Zusammensetzung einverleibt wird.

5. Verfahren nach Anspruch 4, dadurch gekennzeichnet, daß 0,05 bis 10 Gew.-% des Polyamids, bezogen auf den Füllstoff, verwendet werden.

6. Verfahren nach Anspruch 4 oder 5, dadurch gekennzeichnet, daß es sich beim Füllstoff um Kohlenstoff-Fasern handelt.

7. Verfahren nach Anspruch 4 oder 5, dadurch gekennzeichnet, daß der Füllstoff unter vollaromatischen Polyesterfasern, organischen Synthesefasern und natürlichen Fasern ausgewählt wird.

Revendications

1. Composition à base de polyester qui comprend un polyester à cristal liquide, 1 à 70 pour cent en poids, par rapport à la composition, d'une charge autre qu'un polyamide, et 0,05 à 10 pour cent en poids, par rapport à la charge, d'un polyamide.

2. Composition à base de polyester à cristal liquide selon la revendication 1, dans laquelle la charge est une fibre de carbone.

3. Composition à base de polyester à cristal liquide selon la revendication 1, caractérisée en ce que la charge est choisie parmi les fibres de polyester entièrement aromatique, les fibres synthétiques organiques et les fibres naturelles.

4. Procédé de production d'une composition à base de polyester qui comprend un polyester à cristal liquide et 1 à 70 pour cent en poids, par rapport à la composition, d'une charge autre qu'un polyamide, caractérisé par le fait que la charge a été traitée en surface avec 0,05 à 20 % en poids, par rapport au poids de charge, d'un polyamide et la charge traitée en surface est ensuite incorporée à la composition.

5. Procédé tel que revendiqué dans la revendication 4, caractérisé par le fait qu'on utilise 0,05 à 10 pour cent en poids du polyamide par rapport à la charge.

6. Procédé tel que revendiqué dans la revendication 4 ou 5, caractérisé par le fait que la charge est une fibre de carbone.

7. Procédé tel que revendiqué dans la revendication 4 ou 5, caractérisé par le fait que la charge est choisie parmi les fibres de polyester entièrement aromatique, les fibres organiques synthétiques et les fibres naturelles.